Studies on Acetylene and its Derivatives. (IX) The Catalytic Conversion of Acetaldehyde to Acetone. (3). On Catalysts.

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The Catalytic Conversion of Acetaldehyde to Acetone. (3). On Catalysts.[1]

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This paper presents the investigation of good catalysts in the synthesis of acetone from acetaldehyde and water in vapor phase.

A 30 % aqueous solution of acetaldehyde was dropped at 10cc./hr. into a silica tube at 400° partially stuffed with a metallic oxide. The produced liquid, containing acetic acid, acetaldehyde and acetone, and the gases (CO_2, C_nH_{2n}, O_2, CO, H_2, CH_4 and N_2) formed were analyzed. The conversion ratio of acetaldehyde and the yield of acetone were markedly high with ZnO, CdO, PbO or Fe_2O_3, followed by CaO, SnO_2, or MnO_2. With NiO, the conversion ratio was large, but the yield of acetone was nil. Al_2O_3 showed no effect. With CuO, SnO_2, V_2O_5 or MoO_3, the yield of acetic acid was high as compared with other oxides.

INTRODUCTION

It is well known that acetone is prepared by passing acetaldehyde and water in vapor phase over the catalyst of ZnO[2] Fe_2O_3[3], other metallic oxides, or mixtures of them.[2][3][4]

$$2CH_3CHO+H_2O \longrightarrow CH_3COCH_3+2H_2+CO_2 \quad (I)$$

In this paper, the behaviors of acetaldehyde in gaseous reaction with water over various metallic oxides are presented.

EXPERIMENTAL

1. Apparatus. The apparatus is shown in Fig. 1.

2. Procedure. After the reaction chamber B (length 30 cm, diameter 1.5 cm) had been stuffed with a catalyst (30cc.) and heated at 400°C for 30 minutes, all parts of the apparatus were connected. As soon as a 30% aqueous solution of acetaldehyde (25cc.) began to be charged, water was dropped down from H, so that acetaldehyde and acetone, which could not be condensed in F and G, might be absorbed. The formed gas, led from K in the course of reaction, was analyzed. After all acetaldehyde had been charged, distilled water (10 cc.) was dropped down to expel the products

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in the reaction tube. The mixture of liquids in F, G and J was analyzed.

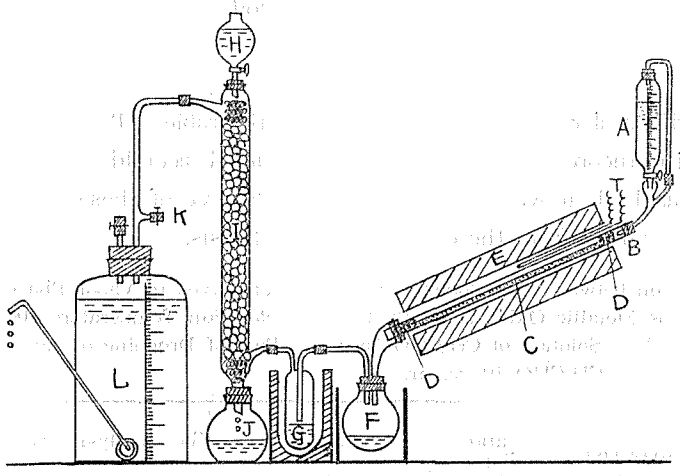

Fig. 1. A : Dropping funnel for aqueous solution of acetaldehyde; B : Silica tube (diameter 1.5 cm); C : Catalyst bed (length 30 cm, volume 30 cc), D : Glass fiber; E : Electric furnace (length30 cm); F : Flask (Cooling with ice and salt); G : Trap (cooling with ice and salt), H : Dropping funnel for water; I : Absorbing tower filled with glass pieces; J : Flask, K : Exit of the formed gas; L : Gas holder, T : Pyrometer

3. Catalysts. As catalysts, CuO, CaO, MgO, ZnO, CdO, Al_2O_3, TiO_2, SnO_2, PbO, V_2O_5, Cr_2O_3, MoO_3, MnO_2, MnO, Fe_2O_3, CoO, NiO were used. The methods of preparation of some catalysts were as follows:

ZnO : Commercial $ZnCO_3$ was decomposed at 500°C for 5 hrs.

CdO : $Cd(OH)_2$, obtained from aqueous solutions of $Cd(NO_3)_2$ and NaOH, was washed thoroughly with water, filtered, dried, and calcined at 500°C for 5 hrs.

PbO : PbO was prepared from $Pb(OH)_2$ by the same method as in CdO and seems probably to contain Pb_3O_4 and PbO_2.

Fe_2O_3 : $Fe(OH)_3$, precipitated from an aqueous solution of $FeCl_3$ and conc. NH_4OH, was washed thoroughly with water, filtered, dried, and calcined at 600°C for 5 hrs.

4. Reaction Conditions. Catalyst, 30 cc.; Length of the catalyst bed, 30 cm; Reaction temperature, 400°C; Volume of the 30% aqueous solution of acetaldehyde, 25 cc.; Rate of dropping of the aqueous solution of acetaldehyde, 10 cc./hr.

5. Analysis of reaction products

(a) Analysis of produced liquid. The produced liquid was diluted to 500 cc. with water, and then acetic acid, acetaldehyde, and acetone were determined by the methods described in the first paper[7] of this series. After a sample of 50 cc. was refluxed for 30 minutes to expel CO_2, acetic acid was determined and for the analysis of acetaldehyde and acetone, a sample of 5 cc. or 10 cc. was taken.

(b) **Gas analysis.** The gases (CO_2, CnH_2n, O_2, CO, H_2, CH_4 and N_2) formed were analyzed by Hempel's and combustion method.

RESULTS

The experimental results are summarized in the table. The yield of acetic acid or acetone is the theoretical value based on consumed acetaldehyde. As the ratio of O_2 to N_2 was 1 : 4, it was considered that the source of these gases was the air, so they were excluded from the column of gas analysis.

Reaction between Acetaldehyde and Water Catalyzed in Vapor Phase by Various Metallic Oxides. (Catalyst 30cc. ; Reaction Temperature 400°C ; 30 % Aq. Solution of CH_3CHO 25 cc. ; Rate of Dropping of Aq. Solution of CH_3CHO 10 cc./hr.)

Exp. No.	Catalyst	Aq. Soln. of CH_3CHO		Conv. Ratio of CH_3CHO (%)	Yield		Gas Analysis (%)					H_2/CO_2
		CH_3CHO (g)	CH_3COOH (g)		CH_3COOH (%)	CH_3COCH_3 (%)	CO_2	CnH_2n	CO	H_2	CH_4	
1	None	7.616	0.065	14.5	—	0	2.9	0	44.0	6.1	47.0	—
2	CuO	6.695	0.076	43.8	38.1	21.0	66.0	0.4	5.8	25.9	1.9	—
3	CaO	7.618	0.112	54.9	—	29.5	0	0	6.6	93.4	0	—
4	MgO	7.900	0	42.3	—	7.5	20.0	0	23.5	41.2	15.3	2.06
5	ZnO	6.498	0.196	87.8	—	74.0	33.0	0.9	1.6	64.5	0	1.96
6	CdO	7.863	0.123	77.6	—	69.6	46.0	4.5	1.8	43.2	4.5	—
7	Al_2O_3	8.023	0.092	16.5	—	0	4.6	0.5	40.4	14.7	39.8	—
8	TiO_2	7.820	0.045	30.2	—	5.6	13.6	0	27.2	33.9	25.3	2.49
9	SnO_2	7.115	0.102	56.0	13.4	29.2	41.1	12.0	5.8	35.0	6.1	—
10	PbO	7.688	0.063	87.3	—	71.7	43.7	0.5	0.8	52.9	2.1	—
11	V_2O_5	7.445	0	62.6	20.4	18.2	41.0	1.3	43.6	14.1	0	—
12	Cr_2O_3	7.478	0.048	40.0	—	21.5	37.9	0.7	7.7	49.3	4.4	—
13	MoO_3	7.370	0	35.5	65.9	32.4	16.9	0	53.2	23.4	6.5	—
14	MnO_2	8.005	0.105	77.3	—	23.4	91.4	0.2	0.3	7.3	0.8	—
15	MnO	6.973	0.114	43.4	—	32.0	—	—	—	—	—	—
16	Fe_2O_3	6.463	0.258	95.7	—	80.3	36.8	1.3	0.3	61.6	0	1.67
17	CoO	7.445	0.125	28.7	—	14.0	58.6	0	24.2	8,7	8.7	—
18	NiO	7.310	0.019	100.0	—	0	37.6	0	2.0	48.4	12.0	—

Then, actions of the catalysts are considered.

No catalyst : Conversion ratio was 14%, but no acetone was produced. As the formed gas was almost composed of CH_4 and CO, the decomposition of acetaldehyde seems to be the main reaction.

CuO : The yield of acetic acid was 38%. The ratio of H_2 to CO_2 was smaller than 2, and the black color of CuO turned red. This seems to show the reduction of the catalyst.

CaO : The yield of acetone was 29%, acetic acid was not obtained and the formed gas was almost consisted of H_2. Since acetic acid and carbon dioxide were fixed on

catalyst as calcium acetate and calcium carbonate respectively, those results seem to be probable.

ZnO : The conversion ratio was 87% and the yield of acetone was 74%. The ratio of H_2 to CO_2 was about 2. So the normal reaction of formula (I) occurred mainly and no side reaction.

CdO : The conversion ratio was 77% and the yield of acetone was 69%. It seems due to the reduction of the catalyst that the ratio of H_2 to CO_2 was smaller than 2. The brown color of CdO turned yellow.

Al_2O_3 : The catalytic action was not found, as in the case of no catalyst.

PbO : The conversion ratio and the yield were 87% and 71% respectively. It seems due to the reduction of the catalyst that the ratio of H_2 to CO_2 was smaller than 2. The orange color of the catalyst turned yellow.

V_2O_5 : The yield of acetic acid was 20%. The yellowish-brown color of the catalyst turned black.

MoO_3 : The yield of acetic acid was the maximum of 66%.

Fe_2O_3 : The conversion ratio was 95% and the yield of acetone was the maximum of 80%. The ratio of H_2 to CO_2 was about 2.

NiO : The conversion ratio was 100%, but the yield of acetone was nil and the yield of acetic acid was very low. The quantity of formed gas was very large, and acetaldehyde seems to be decomposed mostly to gaseous substances. The black color of the catalyst turned light green, so the catalyst seems to be reduced.

SUMMARY

Passing a 30% aqueous solution of acetaldehyde in vapor phase over the various metallic oxides at 400°C, the following results were obtained :

(1) The conversion ratio of acetaldehyde and the yield of acetone were markedly high with ZnO, PbO or Fe_2O_3, followed by CaO, SnO_2 or MnO_2 ;

(2) with NiO, the conversion ratio was high but the yield of acetone was nil.

(3) Al_2O_3 showed no effect ;

(4) with CuO, SnO_2, V_2O_5 or MoO_3, the yield or acetic acid was high as compared with other oxides.

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